bound cytosine nucleobases were considered independent binding sites for the partners; association constants were determined in analogy to the method described in reference [2a]. For **3** $K = 10.0 \pm 1.7\,\text{M}^{-1}$ (3σ) corresponds to the weighted mean of the individually calculated association constants of the NH_2 ($K = 10.14 \pm 2.37\,\text{M}^{-1}$, $\delta_0 = 6.472 \pm 0.023$, $\delta_\infty = 7.432 \pm 0.055$; the index 0 denotes a high dilution, the index ∞ denotes a high concentration) and N1H ($K = 9.89 \pm 2.51\,\text{M}^{-1}$, $\delta_0 = 10.576 \pm 0.051$, $\delta_\infty = 12.541 \pm 0.125$) protons of 9-EtGH. Since NH_2 of cytosine could not be detected at higher concentrations, only a rough estimate of K could be obtained; however, this value was, within the given error limits, in agreement with that for the guanine protons.

An equimolar solution of **2** (120 mM) and 1-MeC was stepwise diluted and ^1H NMR spectra were recorded. The association constant $K = 24 \pm 8\,\text{M}^{-1}$ corresponds to the weighted mean of the individually calculated association constants of the N3H(C) ($K = 37.8 \pm 14.0\,\text{M}^{-1}$, $\delta_0 = 11.899 \pm 0.035$, $\delta_\infty = 13.127 \pm 0.143$), $N4H_2$(1-MeC) ($K = 16.8 \pm 4.0\,\text{M}^{-1}$, $\delta_0 = 6.925 \pm 0.012$, $\delta_\infty = 7.577 \pm 0.046$), and the $N4H_2$(C) ($K = 29.6 \pm 3.7\,\text{M}^{-1}$, $\delta_0 = 7.184 \pm 0.018$, $\delta_\infty = 8.887 \pm 0.059$) protons. It should be mentioned that the N3H(C) resonance is not observable at high concentrations, and the $N4H_2$ resonance of the Pt-bound cytosine is split into two resonances of which only one is concentration-dependent. Since water of crystallization had not been removed in either case, we consider the reported association constants as lower limits, as the water molecules present in solution will compete for the hydrogen bonding sites.

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[5] Crystal structure data for **3**: $C_{12}H_{27}N_9O_{6.5}Pt_{0.5}$, $M_r = 498.97$, triclinic, space group $P\bar{1}$, $a = 8.949(2)$, $b = 11.177(2)$, $c = 11.889(2)$ Å, $\alpha = 101.06(3)$, $\beta = 103.87(3)$, $\gamma = 113.07(3)^\circ$, $V = 1006.3(3)$ Å^3, $Z = 2$, $\rho_\text{calcd} = 1.647\,\text{g}\,\text{cm}^{-3}$, $\text{Mo}_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $\mu = 3.566\,\text{cm}^{-1}$, $T = 298$ K. A total of 7013 reflections (3526 unique, $R_\text{int} = 0.0238$, $\theta < 25.63^\circ$) were collected on a Nonius KappaCCD diffractometer. The structure was solved by patterson synthesis (G. M. Sheldrick, SHELXS-86, **1990**) and refined by full-matrix least-squares on F^2 values of 3476 reflections with $F_o^2 > 2\sigma(F_o^2)$ (G. M. Sheldrick, SHELXL-93, **1993**) to give $wR2 = 0.0621$ and $R1 = 0.0268$ for 286 parameters. Residual electron density max/min $0.508/-0.853\,\text{e}\,\text{Å}^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-162162. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Electrochemical Regeneration of Low-Valent Indium(I) Species as Catalysts for C–C Bond Formations[**]

Gerhard Hilt[*] and Konstantin I. Smolko

Dedicated to Professor Martin F. Semmelhack
on the occasion of his 60th birthday

In recent years the chemistry of indium has become more popular in organic synthesis, partly due to the ability to perform this chemistry in water or aqueous solvent systems. The chemistry of indium metal as well as the chemistry of indium salts for C–C bond formation processes has been reviewed several times.[1] In most cases indium metal is used in stoichiometric amounts and only in a few cases could versions be realized that were catalytic in indium, accompanied with a stoichiometric amount of a reducing agent.[2] In addition, the chemistry of low-valent indium(I) salts has been sparsely investigated, most probably because of the high cost of these species.[3]

Our approach to an electrochemical regeneration process for low-valent indium species was based on the idea of using the cathode as the reducing agent for the spent indium(III) reagent (Scheme 1). We chose the indium-catalyzed allylation of benzaldehyde with allyl bromide as a test reaction. We found, however, that an efficient allylation only took place when sacrifical anodes (preferably aluminum foil anodes)[4] were used in an undivided cell, whereas the reaction proceeded only with low conversions when a divided cell (Pt cathode and Al anode) or a quasi-divided cell (Pt foil cathode and Pt wire anode)[5] were used. We concluded that a major part of the reduction process in an undivided cell must

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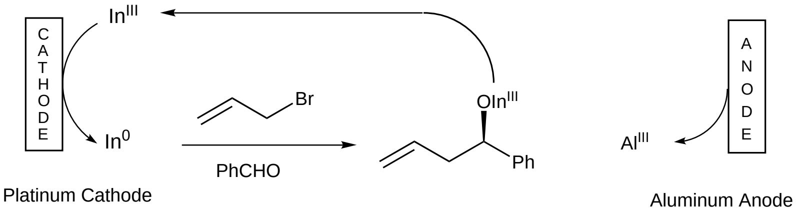
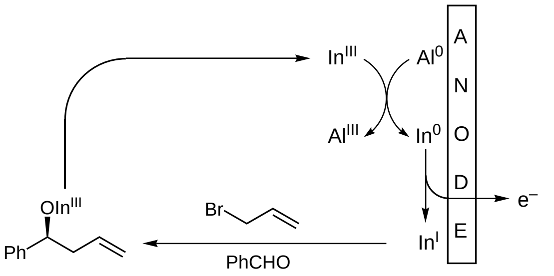


Scheme 1. Planned cathodic reduction of indium(III) salts in the presence of a sacrificial anode.

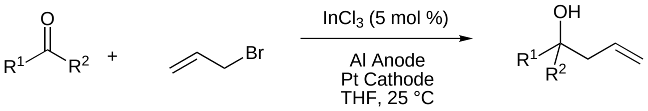
therefore take place at the anode and not at the cathode as originally envisaged.

In the absence of $InCl_3$, however, we detected some conversion under electrochemical conditions, but the rate of the reaction was a factor of 10 – 15 slower than in the presence of indium salts (5 mol% $InCl_3$). The use of aluminum foil as a sacrifical anode leads to the removal of the passivation oxide layer leaving fresh aluminum behind,[6] which is in turn able to reduce the indium(III) salts efficiently to metallic indium. However, deposition of metallic indium in the absence (or at low concentrations) of substrates could not detected, since the polarization as anode causes a reoxidation of the indium metal to THF-insoluble indium(I) salts, which precipitate as orange-brown materials on the electrode surface. Raman spectroscopy and atom emission spectroscopy suggests that this precipate could be $InAlBr_4$.[7] Direct reduction of the indium(III) salts to indium(I) salts, which are sparingly soluble in THF, by the aluminum foil can be excluded since the characteristic brown/red-brown precipitate is not formed under nonelectrochemical conditions. The generation of such low-valent indium species most likely proceeds by the reduction of indium(III) salts to metallic indium, as described for many non-noble metals, followed by reoxidation to indium(I) salts (Scheme 2).[8] The resulting $\mathrm{In^I}$ undergoes oxidative addition to the allyl bromide and, in turn, mediates the formation of the new C–C bond in an indium-catalyzed Barbier-type reaction.



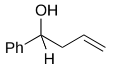
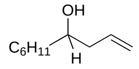
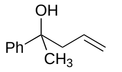
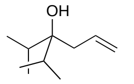
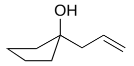
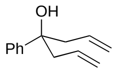
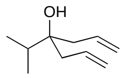
Scheme 2. Reductive anodic process for the generation of low-valent indium species at the aluminum anode for the electrochemical allylation of benzaldehyde.

Preparative reactions with different types of aliphatic and aromatic carbonyl compounds, and even sterically demanding ketones (Scheme 3), were carried out under these electrochemical conditions, and some characteristic examples are given in Table 1 (entries 1 – 5). The electrolyses were conducted under galvanostatic conditions (100 mA) until 1.0 $\mathrm{F\,mol^{-1}}$ of current was consumed. The conversions were in all cases complete (with the exception of the reaction in entry 4, Table 1), but the current yield for the conversions of simple aldehydes and ketones often exceeded 100% during the course of the reaction, which suggests that a chemical side reaction, which is most probably based on allylations mediated by indium or aluminum metal, cannot be discarded completely.

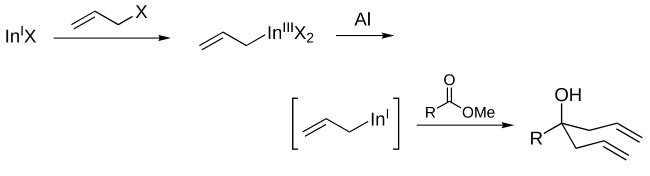


Scheme 3. Catalytic allylations of carbonyl compounds under electrochemical conditions.

Table 1. Results of the electrochemical indium-catalyzed allylations of carbonyl compounds.

Entry	R^1	R^2	Product	Yield [%]
1	Ph	H		89
2	C_6H_{11}	H		76
3	Ph	CH_3		96
4	*i*Pr	*i*Pr		50
5	-$CH_2CH_2CH_2CH_2$-			87
6	Ph	OCH_3		85
7	*i*Pr	OCH_3		82

Of special interest are bis-allylations of aromatic and aliphatic esters (Table 1, entries 6 and 7), since such conversions cannot be achieved by using conventional stoichiometric allylations of the ester by means of indium metal or indium(I) iodide.[9] A bis-allylation of carboxylic esters can, however, be conducted in relatively low conversion using stoichiometric amounts of allylaluminum sesquibromide (<30% after 2 h). Also, a bis-allylation of carboxylic esters with stoichiometric amounts of $InAlBr_4$ or a mixture of $\mathrm{In^IBr}$ and $AlBr_3$ is not observed. In contrast, the desired product can be obtained when preformed stoichiometric amounts of allylindium sesquibromide or allylindium dihalide are treated with aluminum powder under sonication conditions (>70% conversion after 2 h, Scheme 4). Evidently, allylindium(III) species are not able to allylate esters and therefore a further reduction step, most likely to reactive, low-valent indium species, is necessary to generate a more powerful allylating agent which can complete the desired conversion. Another observation supports these findings; when freshly prepared allylmagnesium halides are treated with indium(I) iodide in THF at −40 °C, the desired bis-allylated product can be

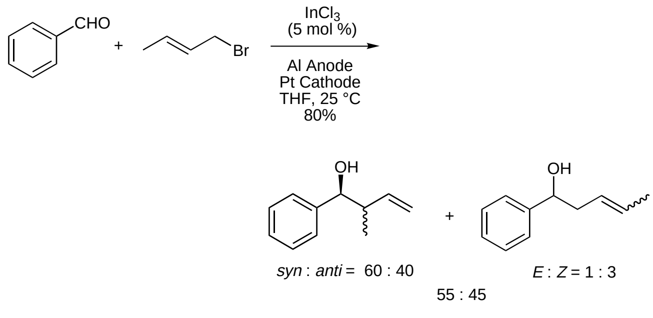


Scheme 4. Reductive activation of allylindium(III) intermediates in the electrochemical allylation of carboxylic esters.

obtained. Thus, a freshly prepared solution of allylmagnesium halide was added at −78 °C to a red-purple suspension of In^{I}I in THF, and upon warming to −40 °C a clear solution was obtained. After the addition of the ester the solution was stirred for 10 min. Subsequent analysis indicated that the conversion was 80 %.[10] For the conversion of aldehydes and ketones, however, the initially formed allylindium(III) species seems to be sufficiently reactive to facilitate an effective allylation process, without the need for further reduction of the allylindium(III) dihalide.

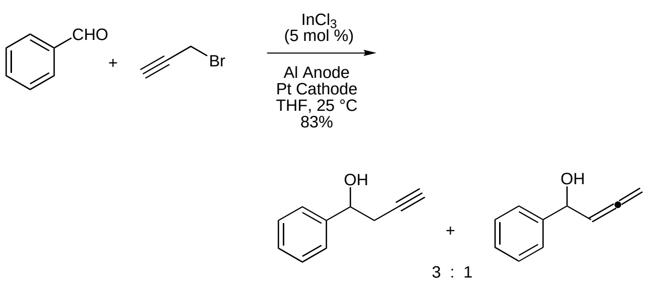
Moreover, in the presence of the supporting electrolyte (0.1M Bu_4NBr) the formation of Lewis acidic AlX_3 compounds is suppressed, and AlX_4^- ions are formed immediately, and thereby the possible Oppenauer-type oxidation of the generated homoallylic alcohols to β,γ-unsaturated ketones (Table 1, entry 1) and a subsequent second allylation to bis-allylated products are not observed as a side reaction under the electrochemical conditions.[3b]

Another indication that the allylation process proceeds via indium(I) species formed on the anode is the reaction of crotyl bromide with benzaldehyde, probably one of the few reactions for which it is possible to differentiate between the nature of the allylating agents involved in the process. Presumably, when starting from indium(I) iodide, allylindium dihalides are generated, whilst the reaction of indium metal furnishes allylindium sesquihalides as the allylating agent. Analysis of the products from the crotylation of benzaldehyde mediated by indium(I) halides gives a mixture of the four possible stereoisomers (γ-substitution product: *syn*/*anti* isomers; α-substitution product: *E*/*Z* isomers).[3] In contrast, when the crotylation of benzaldehyde is performed starting from indium metal the γ-substitution product is formed exclusively under otherwise identical reaction conditions.[11] In our electrochemical crotylation of benzaldehyde we found the product distribution is almost identical with that obtained in the indium(I)-mediated crotylation (Scheme 5). A transmetalation of the allyl group from indium to aluminum can also be excluded since both the stoichiometric crotylation using preformed allylaluminum sesquihalides, as well as the relatively slow electrochemical reaction in the absence of indium(III) salts, also furnishes the γ-substitution product exclusively.



Scheme 5. Catalytic crotylation of benzaldehyde under electrochemical conditions.

Further support for the involvement of indium species and not aluminum-derived C–C bond formation is provided by the electrochemical reaction of propargyl bromide with benzaldehyde, which gives, under electrochemical conditions, a mixture of the corresponding homopropargylic alcohol and the allenylic alcohol in a ratio of 3:1 (Scheme 6), while an electrolysis in the absence of indium gave no desired product.[12] When the analogous propargylation was performed starting from metallic indium in aqueous methanol a similar product distribution was found (6:1),[13] but when we changed the solvent system to THF, the propargylation with metallic indium gave a complex mixture of products.



Scheme 6. Catalytic propargylation of benzaldehyde under electrochemical conditions.

These findings indicate that in the case of propargylation, the reaction does not proceed via aluminum species or via indium sesquibromides, but that reactive low-valent indium species are formed by a combination of chemical redox processes with metallic aluminum and electrochemical reactions at the anode.

In conclusion, we have achieved for the first time an electrochemical method for generating and regenerating highly reactive low-valent indium(I) species. The particularly unusual feature of these reactions is that the indium salts are reduced at the aluminum anode. Through a combination of an electrochemically activated aluminum surface for the reduction of the indium(III) salts and the anodic oxidation of the resulting metallic indium to indium(I) aluminum halides, In^I-catalyzed allylations could be carried out for the first time. The development of these regeneration routes for low-valent indium(I) species has facilitated catalytic allylations on a preparative scale with aldehydes, ketones, and, for the first time, even carboxylic esters as carbonyl components.

Experimental Section

1-Phenyl-3-buten-1-ol (representative procedure): In a 50-mL beaker cell benzaldehyde (212 mg, 2.0 mmol), allyl bromide (605 mg, 5.0 mmol, 2.5 equiv), indium trichloride (22 mg, 0.1 mmol, 5.0 mol %), and tetra-*n*-butylammonium bromide (0.1M) were dissolved in dry THF (20 mL) under a nitrogen atmosphere. The solution was electrolyzed at constant current (100 mA) until 1.0 F mol^{-1} was consumed on an aluminum foil anode (6 cm^2) and a platinum foil cathode (6 cm^2). After the electrolysis, the solution was stirred for another 10 min and the solvents were removed on a rotary evaporator. The residue was taken up in water and extracted three times with diethyl ether. The organic phase was dried over sodium sulfate and concentrated. The crude product was purified by column chromatography on silica gel (eluent pentane/diethyl ether 10/1) and the product was obtained as a colorless oil (260 mg, 1.78 mmol, 89% yield).

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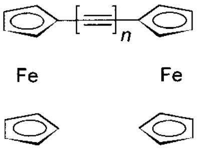
Synthesis and Properties of the First [4.4]Ferrocenophane-1,3,15,17-tetrayne**

Kai H. H. Fabian, Hans-Jörg Lindner,
Norbert Nimmerfroh, and Klaus Hafner*

*Dedicated to Professor Siegfried Hünig
on the occasion of his 80th birthday*

In recent years transition metal complexes of π-conjugated oligomers and polymers have become of increasing interest as potential materials for technical applications.[1] Studies of novel model compounds such as the bisferrocenes **1a–c** and the ferrocenophanes **2a, b** with defined geometric arrangement of the metal atoms have demonstrated that the physical properties of these complexes are determined predominantly by the extent of delocalization and by the electronic interactions between the metal centers.[2,3] In this context the ferrocenophane **2c** with two butadiynyl bridges, homologous with **2a**, **b**, is of particular interest, yet all attempts to prepare it by the oxidative coupling of 1,1′-diethynylferrocene **3c** have been unsuccessful because of its pronounced tendency towards polymerization.[4, 5]



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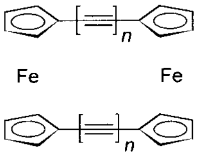
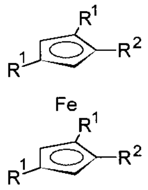


2	a	b	c
n	0	1	2



3	a	b	c	d
R^1	H	*t*Bu	H	*t*Bu
R^2	H	H	≡	≡

The synthesis of the stable 2,2′,4,4′-tetra-*tert*-butyl-1,1′-diethynylferrocene **3d** and its Eglinton coupling[6] has allowed access to the kinetically stabilized derivative **6** of [4,4]ferrocenophane-1,3,15,17-tetrayne **2c**[7a] for the first time.

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